HIGH TEMPERATURE OXIDATION OF IRRADIATED LIMERICK BWR CLADDING*

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Abstract

High-temperature steam-oxidation studies have been conducted using Zircaloy (Zry) cladding samples as part of the High Burnup Cladding Performance program. These data will be used to support modeling and experimental efforts to assess licensing criteria for high-burnup-fuel Loss of Coolant Accidents. Limerick BWR fuel rods (≈57 GWd/MTU) and H. B. Robinson PWR fuel rods (≈67 GWd/MTU) are being used for these studies. Steam-oxidation tests have been completed on archival and irradiated Limerick Zry-2 cladding at 1000-1204˚C for test times ranging from 5-100 minutes. Based on total sample weight gain, no significant difference in oxidation kinetics has been observed between irradiated and unirradiated Zry-2 samples. Both sets of results are in good agreement with the Cathcart-Pawel best-estimate model predictions, as well as data from irradiated (≈49 GWd/MTU) TMI-1 Zry-4 tests at ≈1200˚C. Metallographic analysis, which is more accurate than direct sample weight gain, has been used to determine the oxide, alpha and beta layer thicknesses, along with the weight gain, for Zry-2 samples tested at ≈1200˚C. These data are in excellent agreement with the model predictions. The primary high burnup effects observed from these studies are the non-uniformity of the alpha/beta interface, the enhanced growth rate of the oxygen-stabilized alpha layer formed at high temperature and the alpha-prime islands precipitated within the prior-beta layer during cooling. Although these have little impact on weight gain, they result in a reduction in the effective beta layer thickness for irradiated cladding. Metallographic analysis is in progress for samples tested at 1000-1100˚C. Future tests will be conducted using high burnup PWR cladding with in-reactor-formed oxide layers of 40-100 μm. The pre-test oxide layers are ≈10 μm for Limerick and ≈30 μm for TMI-1.

Introduction

The High Burnup Cladding Performance program is being conducted at Argonne National Laboratory (ANL) to provide data that support modeling efforts and that assess licensing criteria for Loss-of-Coolant Accident (LOCA) and Reactivity-Initiated Accident (RIA) events involving high burnup fuel rods. The program is sponsored by the USNRC Office of Nuclear Regulatory Research. The Electric Power Research Institute (EPRI) also plays a major role in the program planning and conduct and by supplying the high burnup BWR and PWR fuel rods: seven Limerick BWR fuel rods (≈57 GWd/MTU) and seven H. B. Robinson PWR fuel rods (≈67 GWd/MTU). In addition, two TMI-1 fuel rods (≈49 GWd/MTU) have been provided by EPRI for validation of test methodologies. The major tasks of the program include: fuel and cladding characterization, cladding high temperature steam oxidation kinetics studies, LOCA Integral Tests, and mechanical properties tests. The focus of this paper is on the results of the oxidation kinetics studies and their impact on LOCA Integral Test planning and interpretation of results.

* Work supported by the U.S. Nuclear Regulatory Commission, Office of Nuclear Regulatory Research (RES).

The current LOCA licensing criteria (10 CFR50.46) limit peak cladding temperature to 2200°F (1204°C) and maximum Equivalent Cladding Reacted (ECR) to 17% during high temperature steam oxidation to ensure adequate ductility during the Emergency Core Cooling System (ECCS) quench and during possible post-LOCA seismic events. In addition, NRC Information Notice 98-29 specifies that the ECR should be based on the total oxidation, including oxide layers formed during normal reactor operation. For PWR cladding, high burnup operation may induce coolant-side oxidation thicknesses of ≈100 μm, corresponding to 10-14% ECR. This would leave very little margin for the LOCA transient oxidation. The primary high burnup phenomena that may affect cladding response during ballooning and burst, steam oxidation, quench and post-quench are: loss of load-bearing base metal thickness due to oxidation, hydrogen pickup (≈500 wppm at ≈100 μm oxide thickness) and formation of an inner-surface oxide layer, all during normal operation; the effective thickness and chemistry (i.e., H_2 and O_2 content) of the prior-beta phase layer following steam oxidation and quench; and decreased fuel permeability and the tightness of the fuel-cladding bond. The LOCA Integral Tests will be conducted with high burnup fueled cladding segments in order to include all the phenomena highlighted. However, it is essential that oxidation studies be performed with cladding samples from the high burnup rods to plan the LOCA Integral Test experimental times that will test the adequacy of the current criteria and will determine the failure threshold for fragmentation during quench and/or the nil-ductility threshold following ECCS quench.

The test plan for oxidation studies of high burnup BWR and PWR cladding specifies ranges of temperature (900-1300°C) and test times (0-300 minutes). The two main purposes for these tests are: to provide adequate oxidation data at 1204°C (0-20 minutes) for planning LOCA Integral Test times to achieve ECR values ≤ 30%; and to develop fundamental data for modeling codes on the effects of high burnup operation on high temperature (900-1300˚C) steam oxidation kinetics. Of particular interest is the influence of the in-reactor-formed, coolant-side oxide layer, and associated hydrogen pickup, on the oxidation kinetics and phase boundary evolution during steam oxidation. In order to determine the effects of these parameters on oxidation kinetics, unirradiated archival cladding samples are tested in the same apparatus used to test the high burnup samples. One-sided, outer-surface oxidation tests are conducted to determine directly the effects of the in-reactor-formed oxide layer on the oxidation kinetics.

At the 28th Water Reactor Safety Information Meeting (WRSM), weight gain results were presented for unirradiated Limerick archival Zircaloy-2 tested in steam at 1204˚C for 5-40 minutes [1]. Three independent methods were used to determine weight gain: change in total sample weight normalized to the oxidation surface area, oxygen content determined from metallography and assumed equilibrium oxygen concentrations at the phase boundaries, and change in oxygen content determined from direct LECO measurements. These results were compared to predictions of the Cathcart-Pawel [2] best-estimate model, which includes rate equations for sample weight gain due to oxygen pickup and for increases in oxide, alpha and oxide-plus-alpha layer thicknesses. The models are based on parabolic kinetics due to diffusion. The model rate constants were determined from tests conducted with unirradiated Zry-4 samples with no pre-test oxide layer. Relative to model predictions, the total sample weight gain data were high due to end effects and local regions of non-uniform oxide growth at the cladding outer surface; the weight gains deduced from the metallography at the midplane were in excellent agreement with model predictions; and the weight gains determined from the direct measurement of oxygen concentration near the sample midplane were low due to oxide/alpha material loss during sample preparation. The oxide layer thickness data from the metallography were also in excellent agreement with the Cathcart-Pawel predictions. The presence of non-uniform regions of enhanced oxidation at the cladding outer surface suggested inadequate control of the steam flow rate and the test chamber environment.

Following the 28th WRSM, the oxidation apparatus was redesigned to provide: better control of the test chamber environment and steam flow, as well as higher steam flow rates. With the new apparatus, extensive out-of-cell thermal and oxidation-kinetics benchmark tests were conducted using unirradiated Zircaloy-2 (Zry-2) and Zircaloy-4 (Zry-4) samples. Test temperatures and times ranged from 1000-1204˚C and 5-20 minutes, respectively. Based on the excellent out-of-cell results, the new oxidation apparatus was installed into a hot cell workstation and tests were conducted on irradiated and unirradiated Limerick Zry-2 cladding samples at 1204˚C (5-20 minutes), 1100˚C (10-50 minutes) and 1000˚C (20-100 minutes). Several test were also run at 1204˚C with irradiated TMI-1 Zry-4 cladding.

Cladding Characterization

The archival Limerick tubing has dimensions typical of the GE-11 (9-by-9 fuel rod array) design: outer diameter (OD) of 11.18 mm and thickness of 0.71 mm. The inner ≈0.1 mm of the tubing is a zirconium barrier and the remaining ≈0.6-mm thickness is recrystallized-annealed Zry-2. The oxygen content has been measured to be ≈0.11 wt.%.

The irradiated Limerick BWR cladding samples have been taken from grid span 4 of a fuel rod (F9) irradiated to an axially averaged burnup of 56 GWd/MTU. Based on metallographic examinations, the inner-surface oxide layer is about 10-15 μm. The outer-surface oxide layer varies circumferentially from about 3 μm to 18 μm, with an average value of ≈10 μm. In the regions where the oxide layer is thin, tenacious crud deposits of 5-10 μm are observed. Based on Leco determinator measurements, the oxygen content of the irradiated cladding is 0.70±0.09 wt.% and the hydrogen content is 72±7 wppm. These values include O_2 and H_2 in crud, outer and inner surface oxide layers and the base metal. At room temperature, the hydrogen is in the form of hydrides concentrated at the outer surface (radial), the inner barrier surface (radial) and in the central region of the cladding ("X-shaped" patterns).

Experimental Apparatus

The schematic of the improved experimental apparatus is shown in Fig. 1. All components, except for the control and monitoring system and the furnace power source, are located in one of the Alpha-Gamma Hot Cells. The cell atmosphere is N_2 with a low, controlled O_2 level. The furnace is a 250-mm-long quad-elliptic, focused radiant heater. With the test train positioned within the furnace, the uniform temperature zone is >100 mm. The furnace is centered with respect to the 52.6-mm-ID quartz tube, which contains the test train and the flowing steam. The test train, which holds the sample, is centered relative to the quartz tube by perforated spacer discs. The test train within the quartz tube is purged with an inert gas (Ar) prior to the introduction of steam. The steam flows from the boiler into the quartz tube, which is sealed at the boiler-tube interface, and exits out the top of the system into the cell. Tests were conducted with average steam flow rates of ≈120-140 mg/s (deduced from water consumption). The system is designed to produce one-sided (outer-surface) oxidation of the sample. It is compatible with the LOCA Integral Test Apparatus, which also includes a line to internally pressurize the sample and a line for the water quench. In order to achieve good reproducibility, the quartz tube remains centered in the furnace and the test train is lowered into the tube. The test train is shown in Fig. 2. The 25-mm-long sample is protected from eutectic interaction with the Inconel holder by alumina spacers and zirconia washers. The Inconel test train is threaded inside the sample area to allow compression to be exerted on the washers. It is also perforated to allow an overpressure of near-stagnant Ar within the sample to further inhibit steam ingress. Three Type-S thermocouples (120˚ apart) are welded onto the Inconel outer surface about 13 mm above the sample. One of these is used for furnace control. The remaining two TCs are used to assess the circumferential temperature variation. A fourth thermocouple (not seen in Fig. 2) is suspended within the sample at the sample midplane. This internal thermocouple is used for data analysis.

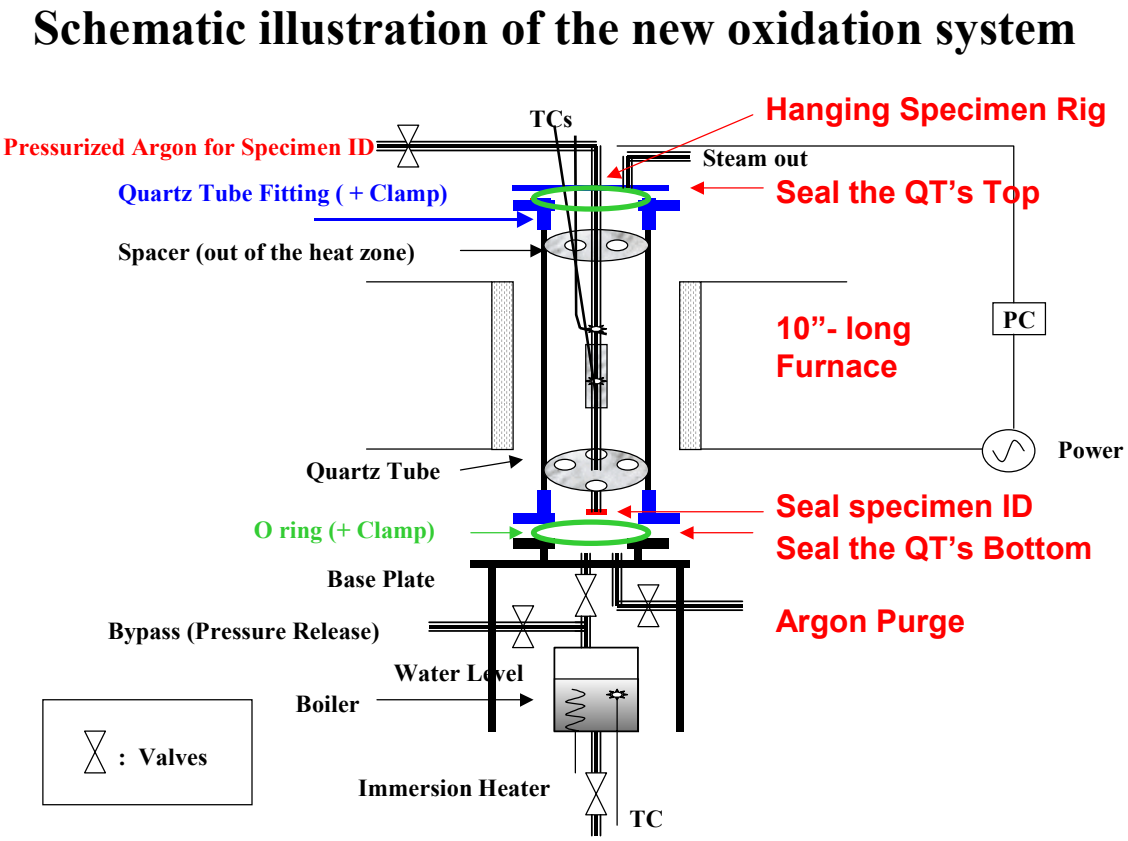

Fig. 1. Schematic of the in-cell steam-oxidation kinetics test apparatus.

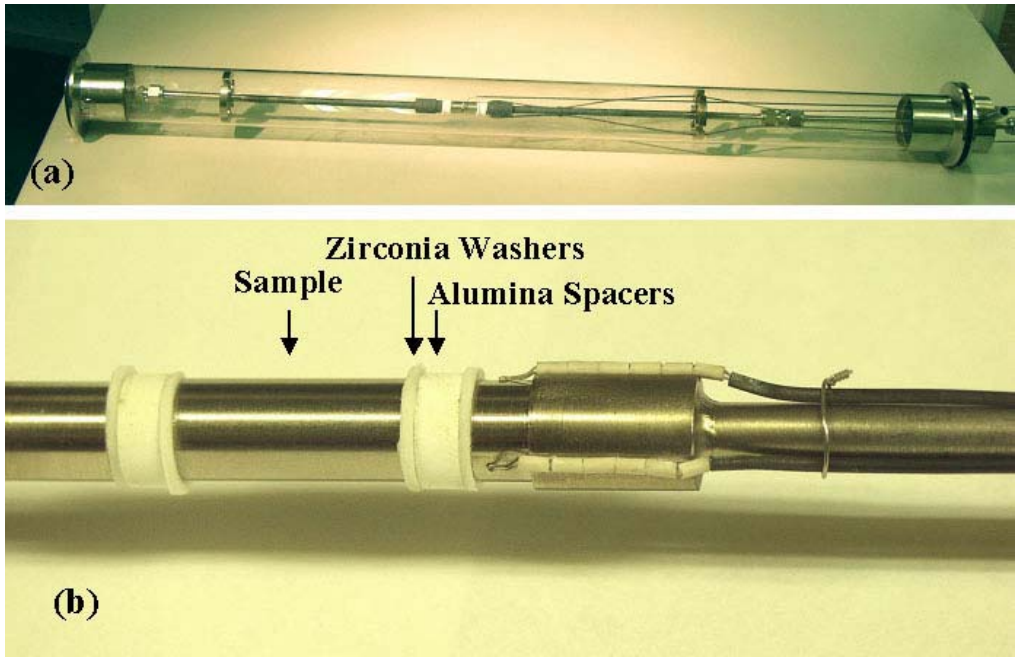

Fig. 2. Test train for in-cell steam-oxidation kinetics studies of Zircaloy cladding: a) test train within quartz tube; b) enlarged view of sample region within the test train.

Test Conditions

Extensive out-of-cell benchmark tests were conducted to ensure adequate temperature control in terms of time history and uniformity of temperature in the circumferential direction. During the course of the benchmark testing, modifications were made to the thermocouple (TC) attachment method and geometry. It was found that excellent reproducibility of results and agreement in readings among the furnace-control TC attached to the Inconel holder, the other two TCs attached to the holder for monitoring temperature variations in the circumferential direction and the internal TC suspended within the sample for data analysis were obtained by: welding the three external TCs to the Inconel and by laying the TC leads as close as practical to the Inconel holder to minimize fin-cooling effects. The design shown in Fig. 2b resulted in reasonably small temperature variations in the circumferential direction and an internal TC reading approximately equal to the average reading of the three external TCs. Additional thermal benchmarking tests were conducted with TCs welded directly onto the outer surface of the sample. Again, the inner TC readings were in excellent agreement with the average of the readings from the TCs welded to the sample. Figure 3 shows the temperature history of the four TCs for the in-cell test LOI-6 with an irradiated Limerick Zry-2 sample at an average hold temperature of 1203˚C for 10 minutes in steam. The response of the internal TC (TC4) lags the control TC (TC2) during the temperature ramp, shows slower cooling after the furnace power is set to zero at the end of the test, but is in very good agreement with the average of the three external TC readings during the hold period.

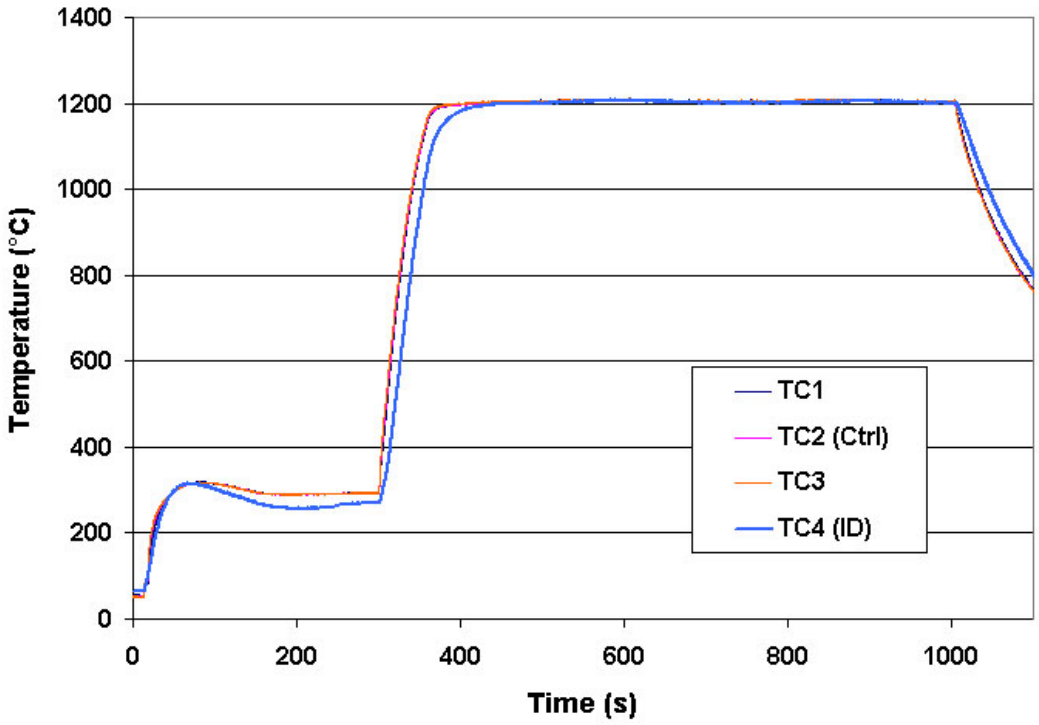

Fig. 3. Thermal response of the four thermocouples during the 10-minute test of an irradiated Limerick Zry-2 sample. The control TC (2) reads 1204˚C during the hold period as programmed. The internal TC (4) reading (1203˚C) agrees well with the average of the 3 external TC readings during the hold time.

The sample identification numbers and test conditions for the in-cell tests are summarized in Table 1. The samples include: unirradiated (archival) Zry-2, irradiated (Limerick) Zry-2 and irradiated (TMI-1) Zry-4. Also shown in Table 1 are the Cathcart-Pawel model-predicted values for weight gain (Δw_p) and the equivalent test time (t_{eq}). The model is integrated over the temperature history recorded by the interior TC (#4 in Fig. 3) to give the predicted weight gain normalized to the exposed surface area (Δw_p). Thus, the ramp-up and ramp-down in temperature are included in the model prediction. The model is used a second time to determine the equivalent time that would give the same weight gain at the steady temperature (T_s). This equivalent time is longer than the hold time because it includes the effects of the temperature ramps. It is a better measure of the time at temperature than the nominal hold time. The degree to which this time is relevant for tests on irradiated cladding with in-reactor-formed oxide layers is determined by the degree to which the weight gain data and oxidation-layer-increase data agree with the model predictions. The measured weight gains (Δw_w) listed in Table 1 were determined by the change (after-test minus before-test) in sample weight normalized to the sample outer surface area exposed directly to the steam. As will be discussed in the next section, these values tend to be higher than predicted because of end effects. Not included in the table are the conditions for, and the results of, the many out-of-cell tests conducted. These tests were conducted in the out-of-cell LOCA Integral Test Mock-up Apparatus (Zry-2 at ≈1204˚C for 10 minutes) and in the out-of-cell Oxidation Test Apparatus (Zry-2 at ≈1204˚C for 5-20 minutes and Zry-4 at 1000-1204˚C for 10 minutes) with and without TCs welded directly onto the sample outer surface. As all the results for unirradiated Zry-2 and Zry-4 have been in good agreement with the Cathcart-Pawel model predictions, especially when the experimental weight gains are determined from detailed metallographic analysis, the emphasis of the in-cell testing has been on the oxidation kinetics of irradiated, high burnup cladding.

Experimental Results

As discussed in Ref. 1, three independent experimental methods are used to assess the sample weight gain and oxygen pickup during high temperature steam oxidation: gross sample weight gain normalized to the sample outer surface area directly exposed to the steam (Δw_w), normalized weight gain based on the increase in oxygen content as determined by the LECO apparatus (Δw_o), and weight gain based on the detailed calculations of the oxygen content within the oxide, alpha and beta layers, whose effective thicknesses are determined though metallographic analysis (Δw_m). In general, the Δw_w values tend to be high because of end effects, the Δw_o tend to be low because some brittle oxide is lost during sample preparation for LECO oxygen determination, and the Δw_m values are the most reliable and accurate.

1. Normalized gross sample weight gain (Δw_w) results

Table 1 lists the Δw_w values determined for the in-cell oxidation tests. These values, along with the values obtained out-of-cell, are plotted vs. the Cathcart-Pawel model predictions (Δw_p) in Fig. 4 (results at ≈1200˚C), Fig. 5 (results at ≈1100˚C) and Fig. 6 (results at ≈1000˚C). Also shown in these figures are the Cathcart-Pawel data (determined from metallographic analysis) used to derive the model. In order to interpret these graphs, points that lie along the 45˚ line would indicate perfect agreement between data and model predictions. Points lying above the 45˚ line indicate that the data are higher than the model predictions, which is the case for the ANL data set. As end effects, including partial oxidation of the sample inner surface, are not included in the surface area used to normalize the ANL data, it is not surprising that the Δw_w results are higher than the model predictions. Metallographic analysis of the extent of the end effects would be needed to adjust the surface area to determine the effective surface area for the normalization. Figure 5 shows these end effects for tests LOI-7 (irradiated Zry-2 in 1204˚C steam for 5 minutes) and LOU-11 (unirradiated Zry-2 in 1204˚C steam for 10 minutes). Although detailed metallographic examinations can be used to correct the data in Table 1 and Figs. 4-6, such examinations

Table 1 Experimental Conditions for the In-Cell Steam Oxidation Tests; unirradiated (U) Zry-2 is archival cladding (11.18-mm OD/9.75-mm ID), irradiated (I) Zry-2 is from Limerick rod F9, and irradiated (I) Zry-4 is from TMI-1 PWR rod H6. Steam flow rate is ≈140 mg/s. "TBC" = To Be Conducted.

Test ID#	Material	Nominal Time minutes	Steady Temperature T_s, °C	Equiv. Time* t_{eq}, s	Predicted (CP-Model) Weight Gain, Δw_p, mg/cm^2	Measured Weight Gain Δw_w, mg/cm^2
LOU-12	Zry-2 (U)	5	1203	343	12.3	14.9
LOU-11	Zry-2 (U)	10	1202	631	16.6	19.9
LOU-13	Zry-2 (U)	20	1205	1250	23.7	26.1
TBC	Zry-2 (U)	10	≈1100	---	---	---
LOU-14	Zry-2 (U)	30	1100	1820	17.0	20.4
TBC	Zry-2 (U)	50	≈1100	---	---	---
TBC	Zry-2 (U)	20	≈1000	---	---	---
TBC	Zry-2 (U)	60	≈1000	---	---	---
TBC	Zry-2 (U)	100	≈1000	---	---	---
LOI-7	Zry-2 (I)	5	1201	373	12.7	14.1
LOI-16	Zry-2 (I)	5	1210	393	13.6	14.0
LOI-6	Zry-2 (I)	10	1203	648	16.9	17.8
LOI-18	Zry-2 (I)	10	1211	631	17.3	17.0
LOI-8	Zry-2 (I)	20	1203	1263	23.6	24.3
LOI-17	Zry-2 (I)	20	1210	1194	23.7	28.1
LOI-9	Zry-2 (I)	10	1098	669	10.2	9.7
LOI-10	Zry-2 (I)	30	1101	1865	17.3	19.8
LOI-11	Zry-2 (I)	50	1100	3076	22.1	24.6
LOI-12	Zry-2 (I)	20	1005	1227	8.1	8.5
LOI-13	Zry-2 (I)	60	1001	3634	13.6	12.9
LOI-15	Zry-2 (I)	100	1000	6092	17.5	21.8
TMI-2	Zry-4 (I)	5	1203	371	12.8	13.2
TMI-1	Zry-4 (I)	10	1201	683	17.2	18.0
TMI-3	Zry-4 (I)	20	1203	1263	23.6	31.1

*$t_{eq} = \exp [20101/(T_s + 273) - 12.8] (\Delta w_p)^2$

would be costly and defeat the main advantages of the sample weight gain approach: data obtained in a simple, fast and reliable manner at very low cost. Given that detailed metallography would be needed to "correct" the sample weight gain data, it would be more useful to do the metallography at the midplane of the sample where the oxide, alpha and beta layers are relatively uniform and representative of the results for these test conditions. For one-sided oxidation tests, such as the ones performed in this study, Δw_w data are used more for screening purposes: excessive weight gains (e.g., factor of 2) may indicate that the test should be repeated rather than be subjected to the more time-consuming techniques of metallographic analysis and/or LECO oxygen determination; and weight gains that are 20-30% higher than model predictions suggest that the mid-planes of the samples should be examined by detailed metallographic analysis to determine weight gains that are independent of end effects. Also, a judgment can be made from the direct sample weight gain data as to whether or not there appears to be significant differences between the oxidation kinetics of irradiated vs. unirradiated cladding. Within the uncertainty of the sample weight gain data in Table 1 and Figs. 4-6, there appears to be no significant difference.

The extent of the "end effects" is dependent on the degree of compression. Zero compression (loose fitting zirconia washers) can result in extensive inner-surface oxidation due to steam ingress. Excessive compression can result in flaring, splitting and heavy oxidation of the ends of the over-constrained sample. Through experience, the pre-test compression can be set within a range that leaves more than ≈80% of the sample free of end effects, particularly those associated with inner-surface oxidation. The experience to date indicates that the end effects extend ≤2 mm from each end of the 25-mm-long sample. Within the remaining 21 mm of the sample, the oxide layers are very uniform, displaying even less thickness variation axially than observed circumferentially at the midplane.

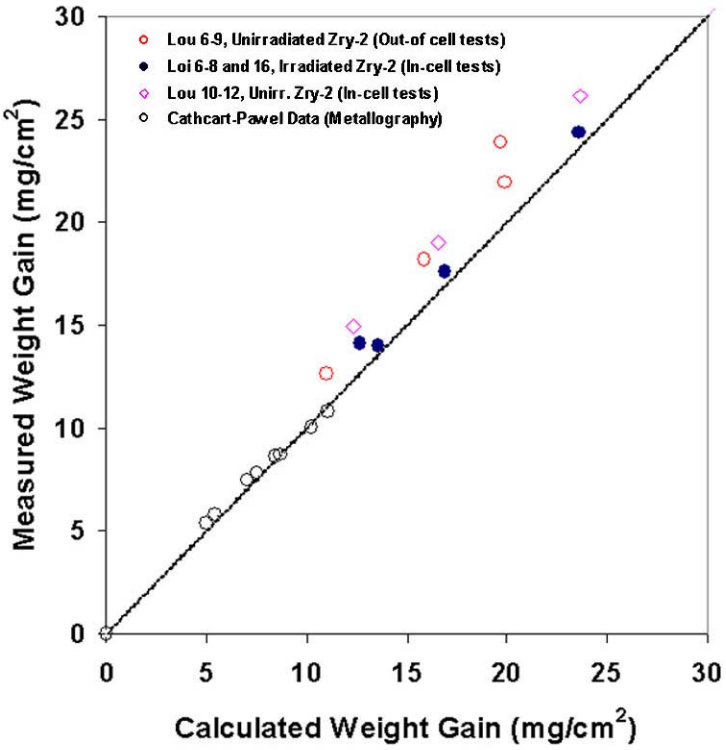

Fig. 4. Comparison of Cathcart-Pawel model predictions (Δw_p) and sample weight gain data (Δw_w) for irradiated (Limerick) Zry-2 and unirradiated (archival) Zry-2 after steam oxidation at ≈1200˚C.

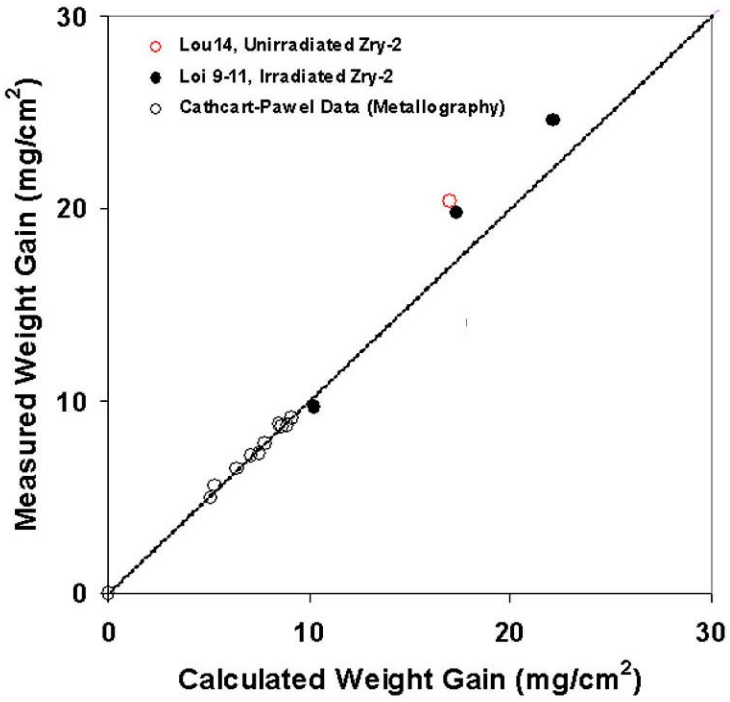

Fig. 5. Comparison of Cathcart-Pawel model predictions (Δw_p) and sample weight gain data (Δw_w) for irradiated (Limerick) Zry-2 and unirradiated (archival) Zry-2 after steam oxidation at ≈1100˚C.

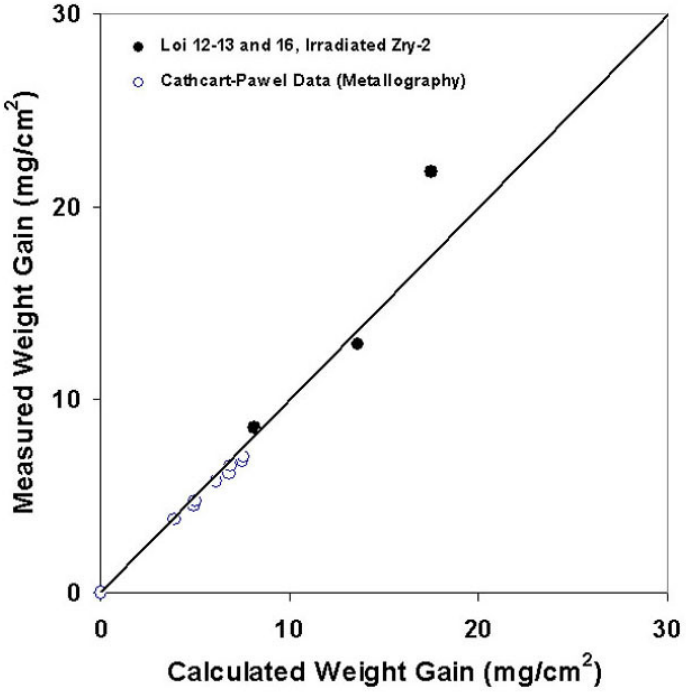

Fig. 6. Comparison of Cathcart-Pawel model predictions (Δw_p) and sample weight gain data (Δw_w) for irradiated (Limerick) Zry-2 after steam oxidation at ≈1000˚C.

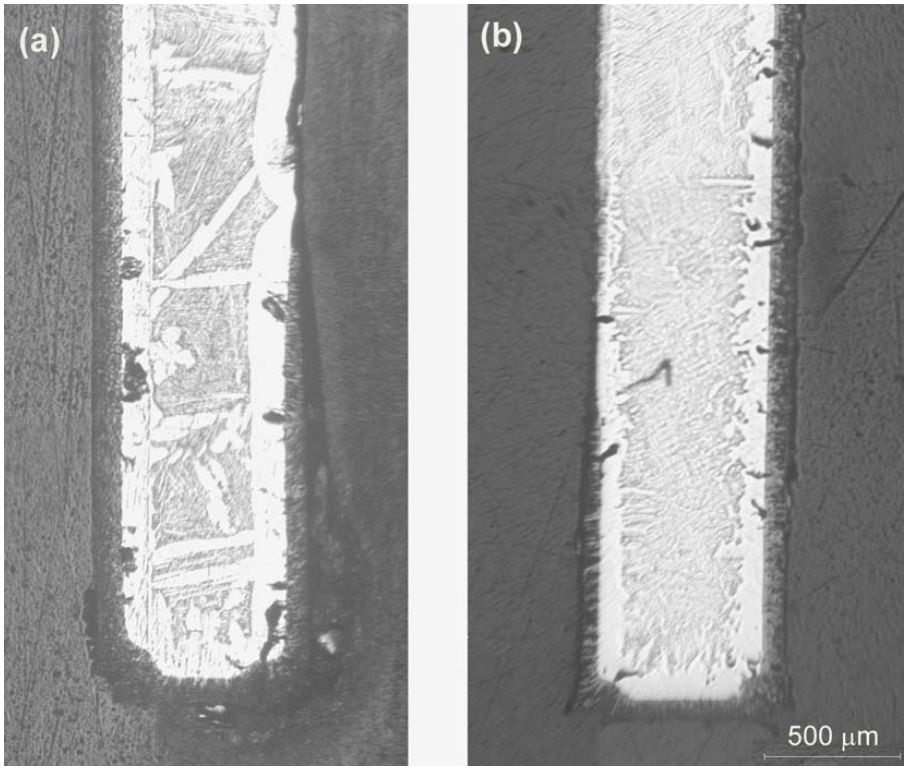

Fig. 7. Oxidation of sample end and partial (<2 mm) oxidation of sample inner surface for (a) LOU-11 test (unirradiated Zry-2 exposed to steam at 1202˚C for 10 minutes) and (b) LOI-7 test (irradiated Zry-2 exposed steam at 1201˚C for 5 minutes).

2. Weight gain determined from LECO oxygen analysis before and after steam oxidation (Δw_o)

Because of the saturation limit of the LECO oxygen determinator, specimens need to be < ≈0.1 g. Specimen preparation involves cutting out a ring ≈3-mm long from near the mid-plane of the 25-mm-long oxidation sample with a wet diamond saw and sectioning it into 4-6 arc lengths. As discussed in Ref. 1, the weight gain deduced from direct measurements of oxygen before and after steam testing tends to fall below the expected value due to partial loss of brittle oxide during specimen preparation. Improvements have been made to both steps in the preparation process to minimize the loss of oxide. In the improved method, the ends of the specimen are ground down to a depth at which the oxide layer is uniform. A wire saw is then used to subdivide the polished ring into ≈0.1-g specimens. These improved specimen preparation techniques have been demonstrated out-of-cell with unirradiated specimens. The results of the LECO oxygen analysis for the better-prepared specimens are compared in Fig. 8 to both the Cathcart-Pawel model prediction and the weight gain determined from metallography for LOCA Test #6 (≈1209˚C for 10 minutes) and LOU-7 (≈1192˚C for 10 minutes). The weight gains deduced from the change in oxygen content (as determined by LECO analysis) are ≈10% lower than the weight gains determined from the metallography. It should be noted that using the previous Ref. 1 techniques for sample preparation gives results ≈25% lower than those deduced from metallography.

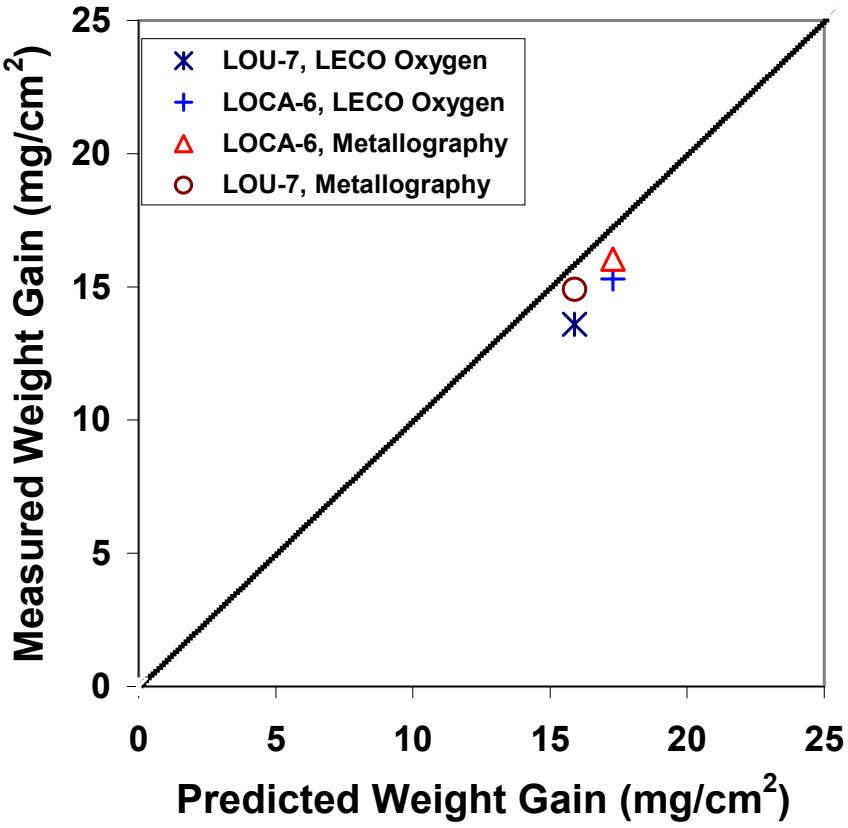

Fig. 8. Comparison of Cathcart-Pawel model predictions for weight gain (Δw_p) with weight gains determined from metallographic analysis (Δw_m) and from the LECO oxygen analysis (Δw_o) after careful specimen preparation to minimize oxide loss. The samples for both LOCA-6 (10 min. in steam at 1209˚C) and LOU-7 (10 min. in steam at 1192˚C) tests are unirradiated (archival) Zry-2.

3. Weight gain determined from metallographic analysis (Δw_m)

This procedure involves metallographic analysis to determine the effective thicknesses of the oxide, alpha and prior-beta layer following steam oxidation of the Zircaloy samples. The thickness of these layers can be compared directly to Cathcart-Pawel model predictions. By assuming "equilibrium" oxygen concentrations at the oxide outer surface (26 wt.% at 1204˚C), at the oxide/alpha interface (24-wt.%/6.7-wt.% at 1204˚C) and at the alpha/beta interface (2.4-wt.%/0.6-wt.% at 1204˚C), as well as a time-dependent diffusion model for the oxide distribution within the layers, the total oxygen increase can be determined. The corresponding weight gain can then be determined and compared to the predicted value. The procedure is straightforward for unirradiated Zircaloy, which is characterized by a negligible outer surface oxide layer and tends to exhibit uniform layer interfaces following high-temperature steam oxidation. More judgment is required in the analysis of irradiated cladding as the in-reactor-formed oxide

layer needs to be defined and subtracted from the total oxide layer observed in the metallographs, and the alpha/beta interface tends to be highly non-uniform due to local regions of enhanced alpha-phase growth.

Based on numerous out-of-cell test results obtained with unirradiated (archival) Zry-2 samples and the more limited test results obtained with unirradiated Zry-4 samples, both the measured oxide layer thickness and the weight gain deduced from the metallographic analysis of oxide/alpha/beta layer thicknesses are in excellent agreement with the Cathcart-Pawel model predictions for steam oxidation tests at ≈1200˚C. Limited data analyzed for specimens tested at 1000˚C and 1100˚C are also in good agreement with the Cathcart-Pawel model predictions. However, more tests at these lower temperatures and more data analyses need to be completed before conclusions for these lower temperatures can be made with confidence. As the focus of this paper is on the test results for irradiated cladding, the results for the unirradiated cladding will be incorporated into the data plots for irradiated cladding.

Figures 9 and 10 show the overview of specimen selection and preparation for metallographic analysis. The midplane cross-section of the sample (25-mm-long, irradiated Limerick Zry-2) for test LOI-6 (10 minutes in steam at 1203˚C) was prepared (e.g., cut, polished, etched) for metallographic imaging. Although the whole cross-section is viewed on the metallograph, eight locations covering ≈45% of the cladding circumference are chosen for detailed analysis. Figure 9 shows the circumferential locations for the eight specimens. Figure 10 represents an enlargement of these metallographic images to highlight the oxide layer at the cladding outer surface. For analysis purposes, each of these images is further enlarged (see Fig. 11) and analyzed using a linear-intercept method and ImagePro Plus software. Three readings of the oxide thickness are taken for each of the eight micrographs. The 24 readings are used to determine the average oxide layer thickness and the standard deviation. For unirradiated material (Fig. 12), the same procedure is used to determine the alpha and beta layer thicknesses because the alpha/beta interface is uniform for unirradiated Zircaloy after high temperature steam oxidation. As can be seen in Fig. 11, this is not the case for irradiated material. Both non-uniformity of the alpha/beta boundary and islands of alpha-prime are observed in Fig. 11. The islands of alpha-prime are formed during cooling and are not important in calculating weight gain as they draw oxygen from the beta layer during cooling. However, the local regions of enhanced oxygen-stabilized alpha phase observed in Fig. 11 are formed during high temperature steam oxidation. Thus, these regions need to be included in the calculation of the effective alpha and beta layer thicknesses for weight gain analysis. Image-Pro Plus software is used to determine the area fractions of alpha and beta in the metallographic images, such as the one shown in Fig. 11.

Figure 13 compares the measured oxide layer thicknesses for unirradiated and irradiated Zry-2 and unirradiated Zry-4 to the values predicted by the Cathcart-Pawel model. The data are for tests conducted at ≈1200˚C in steam for times ranging from 5 to 40 minutes. Included in the figure are the data described in Ref. 1 for unirradiated Zry-2 tested in cell (data points with scatter bars), the out-of-cell data, and the in-cell data. The data plotted in Fig. 13 for irradiated Limerick cladding represents the change in oxide thickness during the steam oxidation. As can be seen in Fig. 14, this requires some judgment. The loose oxide islands that appear disconnected from the main oxide layer are not included in the total oxide. It is assumed that these are oxidized crud. A nominal 10 μm of in-reactor-formed oxide thickness is subtracted from the total oxide layer thickness readings (excluding the loose oxide) deduced from the metallographic image in Fig. 14. Considering that the Cathcart-Pawel model is based on data for unirradiated Zry-4 exposed to ≈1200˚C steam for <5 minutes, the agreement between the extrapolated model predictions and the ≈1200˚C data generated within the ANL program is excellent. As most of the weight gain is contained within the oxide layer, one can expect excellent agreement between the model predictions and the weight gain deduced from the metallography.

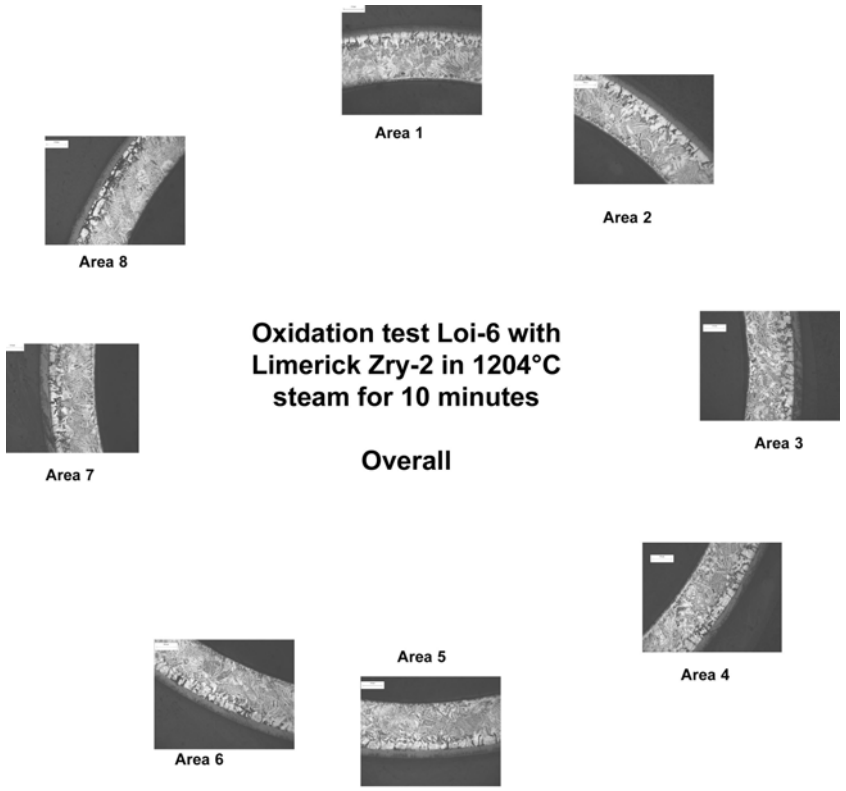

Fig. 9. Circumferential orientation of the eight LOI-6 samples used for metallographic analysis.

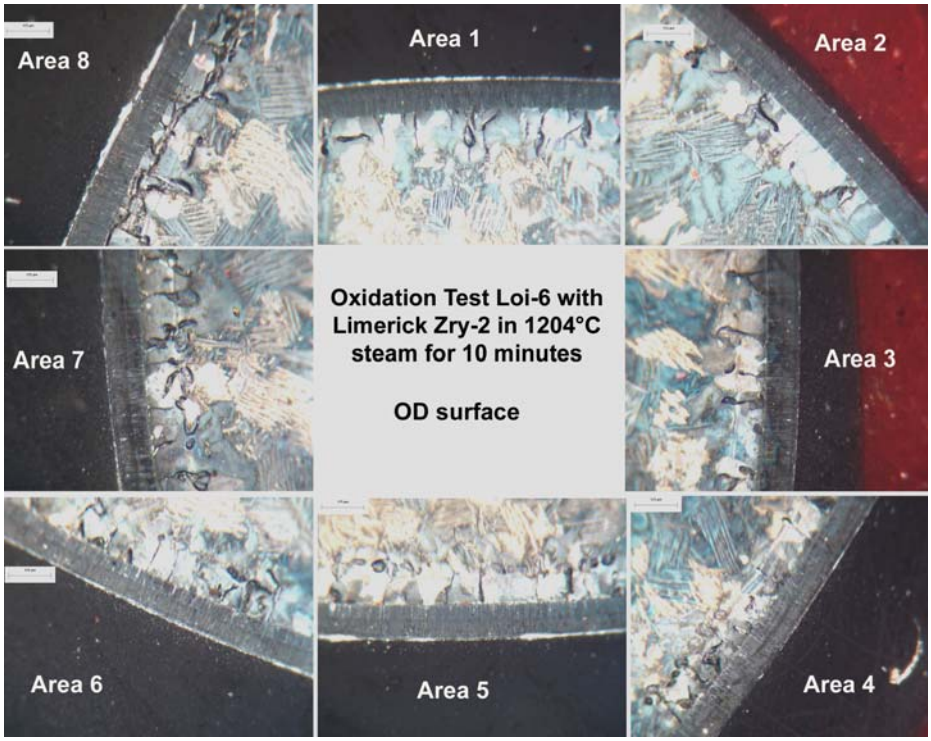

Fig. 10. Oxide layer thickness vs. circumferential location for irradiated (Limerick) Zry-2 LOI-6 test sample.

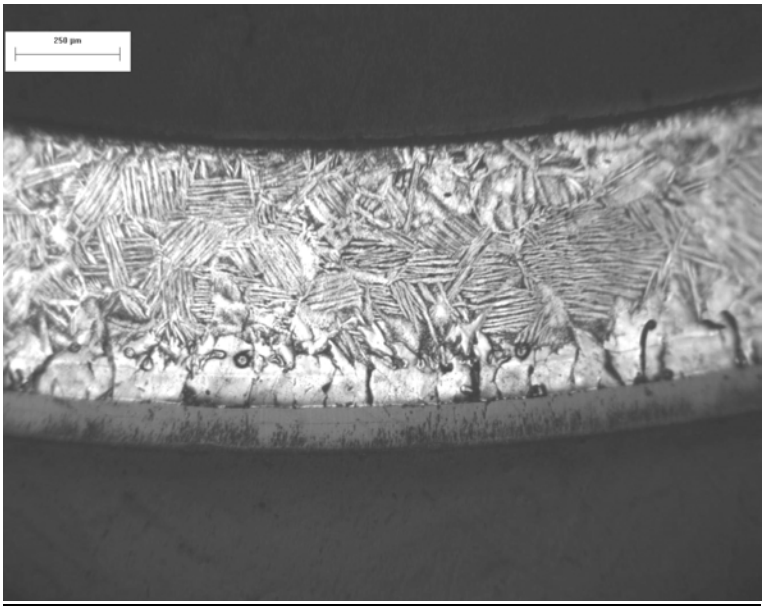

Fig. 11. Etched specimen of irradiated Limerick Zry-2 after 10 minutes exposure to 1204°C steam. Local regions of enhanced growth of the oxygen-stabilized alpha phase are clearly visible.

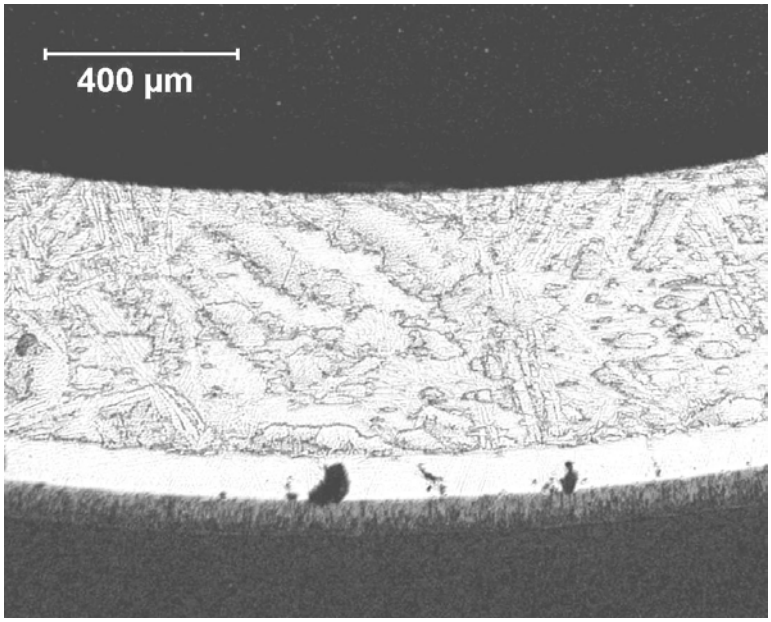

Fig. 12. As-polished specimen of unirradiated archival Zry-2 after 10 minutes exposure to 1192˚C steam. Uniformity of oxide/alpha and alpha/beta interfaces is clearly visible in the unirradiated material.

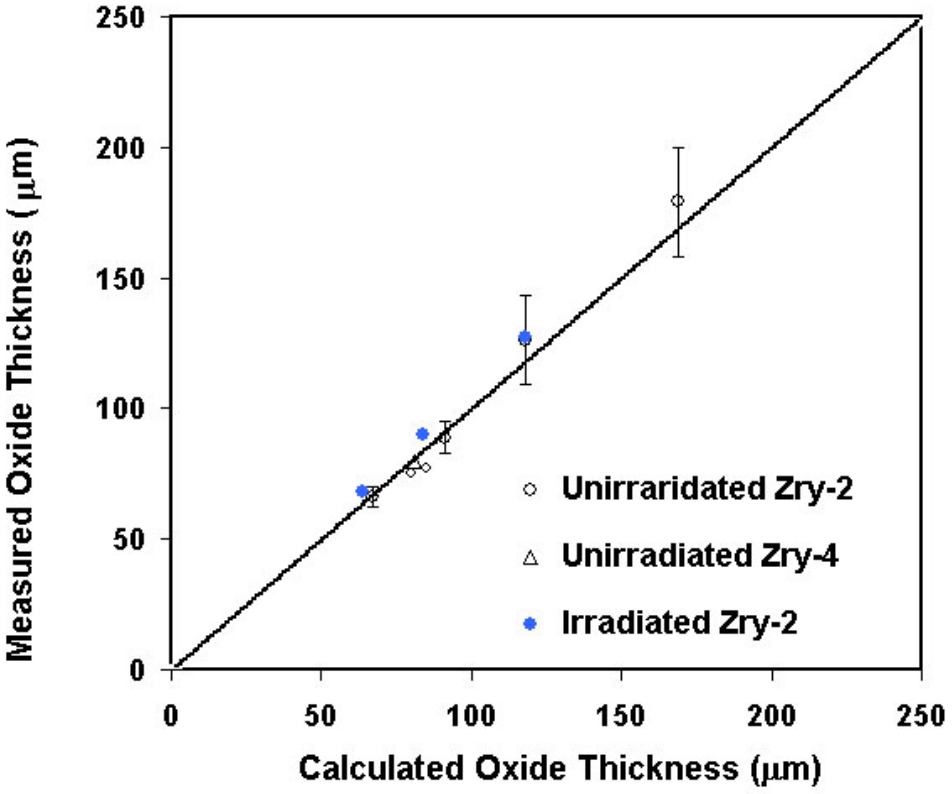

Fig. 13. Comparison of Cathcart-Pawel model predictions and metallographic data for oxide-layer thickness for Zry-2 and unirradiated Zry-4 after ≈1200°C steam oxidation for 5 to 40 minutes.

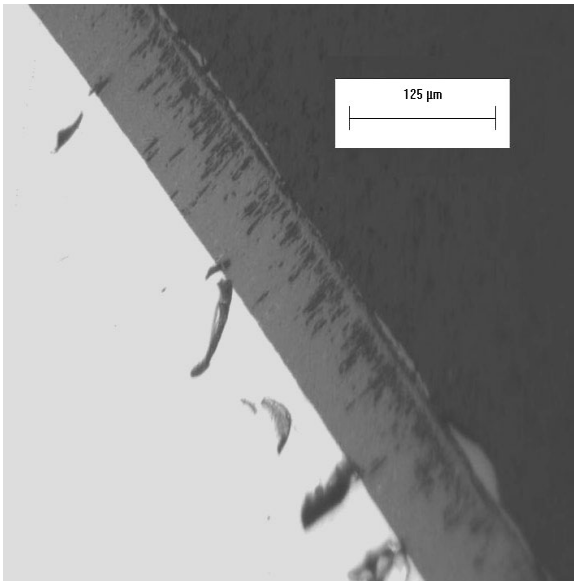

Fig. 14. Enlarged view of the outer-surface oxide layer of irradiated Limerick Zry-2 after exposure to 1204˚C steam for 10 minutes.

Weight gain at ≈1200˚C has been determined from the metallographic images of the unirradiated samples exposed to steam for 5 to 40 minutes and the irradiated (Limerick) samples exposed to steam for 5 to 20 minutes. As shown in Fig.12, the smooth boundaries between the oxide, alpha and beta layers for unirradiated Zircaloy allow for the use of the linear-intercept method for determining oxide, alpha and beta layer thicknesses. The results are shown in Fig. 15 for the Ref. 1 in-cell tests (LOU 1-4) and for out-of-cell tests (LOCA#6, LOU 7-9, and OC#7 Zry-4). Based on the results shown in Fig. 15, excellent agreement is observed between the model predictions and the weight gain data determined from metallographic analysis of unirradiated Zry-2 and Zry-4 and irradiated Zry-2 oxidized in steam at ≈1200˚C. The same good agreement is expected from the in-cell tests conducted on unirradiated Zry-2 samples oxidized in steam at 1000-1200˚C and on irradiated Zry-2 at 1000-1100˚C. These metallographic analyses are in progress

The weight gains determined by metallographic analysis for in-cell ≈1200˚C tests LOI-7 (13.8 mg/cm^2 after 5 min.), LOI-6 (17.8 mg/cm^2 after 10 min.) and LOU-8 (24.4 mg/cm^2 after 20 min.) are only ≈6% higher than the Cathcart-Pawel model predictions and ≈9% higher than the average results for the ≈1200˚C data set for unirradiated samples. The data sets for both the irradiated and unirradiated samples are within the uncertainty band for the model. From a weight gain perspective, the difference of ≈9% between the unirradiated and irradiated samples is not significant. However, as explained in the next section, there are interesting differences in the effective alpha and beta layer thicknesses.

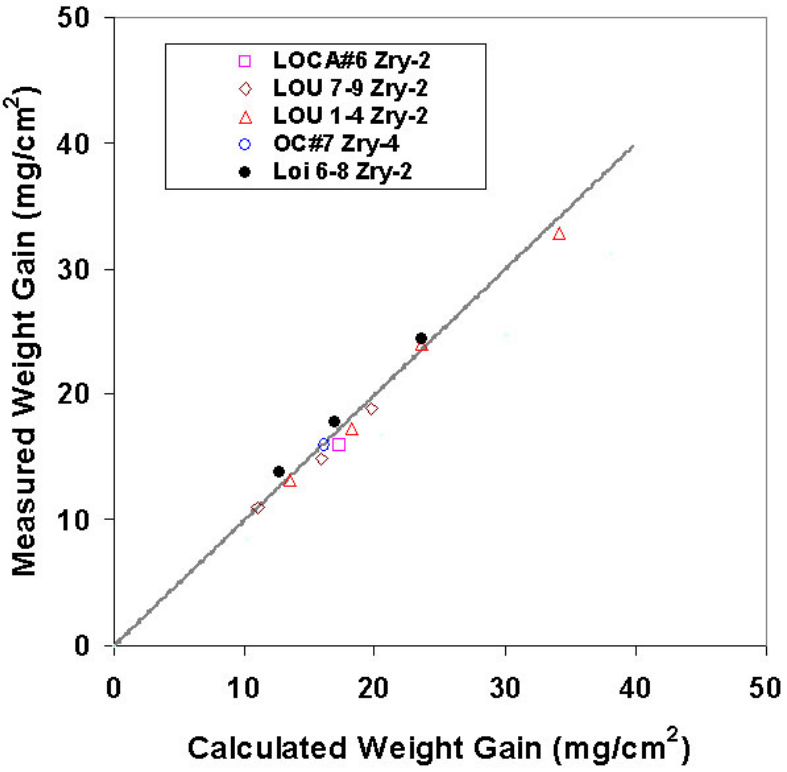

Fig. 15. Comparison of Cathcart-Pawel model predictions (Δw_p) and weight gain data deduced from metallographic analysis (Δw_m) of unirradiated Zry-2 (LOCA#6 and LOU) and Zry-4 (OC#7) and irradiated Limerick Zry-2 (Loi 6-8) samples exposed to steam for 5-40 minutes at ≈1200˚C.

Discussion

One-sided (outer-surface) oxidation tests have been conducted on unirradiated Zry-2 (archival) and Zry-4 and on irradiated Zry-2 (Limerick at 56 GWd/MTU) and Zry-4 (TMI-1 at 49 GWd/MTU) cladding samples. In addition to the many tests conducted out-of-cell on archival Zry-2 and low-tin Zry-4, Table 1 lists the tests that have been completed in cell on unirradiated and irradiated Zry-2 and irradiated Zry-4, as well as the few remaining tests to be completed on unirradiated Zry-2 at 1000˚C and 1100˚C. The decision to use the one-sided oxidation approach, rather than the two-sided approach, was based on several factors: Cathcart and Pawel [2] used this approach to develop the database for their best-estimate model that is used throughout the current work as a basis for comparison; the approach allows for temperature monitoring by means of a thermocouple suspended within the sample; by oxidizing the outer surface, the effects on the oxidation kinetics of the in-reactor-formed, coolant-side oxide layer can easily be isolated and studied; and for the LOCA Integral Tests, most of the 300-mm-long high burnup sample will be exposed only to outer-surface steam oxidation.

Weight gain has been determined by three independent means. Direct measurement of the sample weight before and after the test gives the total weight gain, which is divided by the sample outer surface area, to give the normalized weight gain (Δw_w). These data are ≈5-20% higher than predicted by the Cathcart-Pawel model because end effects result in additional oxidation. This additional oxidation near sample ends has been confirmed by metallography. A better value for the effective surface area that undergoes oxidation could be determined through extensive metallography near the samples ends, but it would not be worth the effort. The simply-obtained Δw_w values are used for: screening purposes to assess the quality of the tests; for comparing the behavior of unirradiated to irradiated Zircaloys; and for demonstrating that the data are more in agreement with the Cathcart-Pawel best-estimate model than with the conservative Baker-Just correlation [3]. The last test in Table 1 (irradiated TMI-1 Zry-4 in steam at 1203˚C for 20 minutes) has an unexpectedly high weight gain (32% higher than model predictions). The metallography at the midplane will be examined very closely to determine whether or not the weight gain deduced from midplane metallographic analysis is also high and, if so, why it is high. The Δw_w data in Table 1 indicate no difference (within the uncertainties of this simplistic approach) between unirradiated and irradiated Zircaloy oxidation kinetics. At 1200˚C the Baker-Just predictions are ≈34% higher than the Cathcart-Pawel predictions. Even though the Δw_w data are artificially high due to end effects, they are lower than the Baker-Just predictions. For irradiated Limerick Zry-2 tests conducted at ≈1200˚C, the average of the weight gains after 5 to 20 minute exposure to steam are only ≈7% higher than the Cathcart-Pawel predictions.

The second method for determining weight gain (Δw_o) is to measure the oxygen content of a sibling sample before the steam-oxidation test and the oxygen content of the test sample after the steam-oxidation test. This approach involves careful preparation of the oxidized specimens for LECO oxygen analysis, as some brittle oxide is lost during the preparation process. To date, significant progress has been made in this area for unirradiated Zry-2. The oxygen content of the as-fabricated cladding is relatively low (≈1100 wppm) and uniform and the cutting and polishing of specimens for LECO analysis can be done carefully out-of-cell. In comparing the weight gains (Δw_o) derived from this approach for unirradiated Zry-2 to those determined from metallographic analysis and from the Cathcart-Pawel model predictions, the values tend to be ≈10% low because some oxide is still lost during the preparation process. However, this is a vast improvement as compared to the techniques and results given in Ref. 1. The old procedure resulted in values that were as much as 25% too low. Work is in progress to apply the new specimen-preparation techniques to irradiated cladding samples.

The third method for determining weight gain (Δw_m) is through metallographic analysis, which is used to measure the effective thicknesses of the oxide, alpha and beta layers after steam oxidation. Using equilibrium assumptions for oxygen content at the oxide outer surface and at the interfaces, along with a time-dependent diffusion model, the oxygen pickup can be determined. This approach is straightforward for unirradiated material, which exhibits smooth interfaces after steam oxidation. For unirradiated Zry-2 tested at ≈1200˚C, the Δw_m values agree with the model predictions to within ≈3%. For irradiated Zircaloy, the procedure is complicated by three factors. A judgment must be made with regard to the outer boundary of the oxide layer, an average in-reactor-formed oxide layer measured from a sibling sample must be subtracted from the total oxide layer thickness observed, and the effective alpha and beta layer thicknesses must be determined from an area averaging approach due to the non-uniformity of the alpha/beta interface. These factors do not have a significant impact on the weight-gain results for irradiated Limerick cladding exposed to steam at ≈1200˚C. The in-reactor-formed oxide layers are small (≈10 μm), and the enhancement in the growth of the alpha region contributes <10% to the overall weight gain. Based on detailed metallographic analysis of the tests conducted on irradiated Zry-2 at ≈1200˚C, the measured oxide layer increases with time are ≈7% higher, the alpha layers are ≈45% thicker and the beta layers are ≈8% thinner than predicted by the Cathcart-Pawel model. Metallographic analysis is in progress to determine the behavior of irradiated Limerick Zry-2 oxidized at 1100˚C and 1000˚C and irradiated TMI-1 Zry-4 oxidized at ≈1200˚C.

Future work is planned to determine the oxidation kinetics of high burnup PWR (H. B. Robinson) Zry-4 cladding under the same test conditions listed in Table 1. The tests will be performed on samples taken from grid span 2 with an in-reactor-formed oxide layer of ≈50 μm and on samples taken from grid span 4 with an in-reactor-formed oxide layer of ≈100 μm. Thus, the full oxidation test matrix includes pre-oxide layers ranging from 10 to 100 μm and hydrogen contents ranging from 70 to ≈500 wppm.

The primary purpose of generating oxidation kinetics data at ≈1200˚C for high burnup cladding is to help plan and interpret the results of the Integral LOCA Tests, which will be conducted with fueled cladding samples at this oxidation temperature. The data obtained to date indicate that exposure times to generate a desired effective cladding reacted (ECR) can be adequately predicted by using the Cathcart-Pawel model. However, weight gain and the associated ECR are not very sensitive measures to determine what is important in ensuring adequate ductility to survive ECCS quench and post-quench events. The effective thickness of the beta layer, its oxygen content and its hydrogen content are the critical factors in determining quench and post-quench ductility. The main difference observed between unirradiated and high burnup Zry-2 behavior is the enhanced growth of the oxygen-stabilized alpha phase in steam-oxidized irradiated cladding. Although this enhancement has little impact on weight gain and ECR, it does result in a reduction in the effective thickness of the ductile beta layer. This assessment requires the use of metallographic analysis and cannot be determined from change in either sample weight or oxygen content. Thus, metallography has two major advantages over the other approaches: it produces the most reliable data for weight gain kinetics and it allows a quantitative determination of the effective beta layer thickness. Work is in progress to determine further reductions in the effective beta layer thickness due to the alpha-prime islands observed within the prior-beta layer.

The effective beta layer thickness following high temperature oxidation in steam is dependent on the cooling rate. Slower cooling will result in a higher fraction of brittle-alpha formation within the prior beta layer and lower ductility of that layer. Based on Fig. 3, the average cooling rate from 1200 to 800˚C is ≈5˚C/s, within the 4-7˚C/s ramp planned for the LOCA Integral Tests. The LOCA tests will have much faster cooling from 800˚C to room temperature than the oxidation tests. However, no significant diffusion and phase changes are expected below ≈800˚C.

Conclusions

High temperature steam oxidation tests have been conducted to determine the oxidation kinetics of high burnup Zircaloy cladding. The tests conducted at ≈1200˚C provide data that will be used to help plan the test times for, and to interpret the data from, the Integral LOCA Tests. The broader range of temperatures in the test matrix (900˚C-1300˚C) will provide data that are important in the analysis of small-to-large break BWR and PWR LOCA events at high burnup. The oxidation tests and post-test analyses completed to date have focused on high burnup Zircaloy-2 (Zry-2) cladding from Limerick BWR rods (56 GWd/MTU), as well as unirradiated (archival) Zry-2 cladding, in the temperature range of 1000˚C-1200˚C. Limited testing has also been completed on irradiated PWR (TMI-1) Zircaloy-4 (Zry-4) cladding, as well as on unirradiated Zry-4, at ≈1200˚C. Additional tests are planned to determine the oxidation kinetics of high burnup PWR (H. B. Robinson at 67 GWd/MTU) Zry-4 cladding.

The results obtained thus far indicate that there are no significant high burnup effects on the weight-gain kinetics of high burnup Zry-2 exposed to steam at 1000-1200˚C. The results are in good agreement with the results for unirradiated Zry-2 (archival) and Zry-4, as well as those predicted by the Cathcart-Pawel model. Detailed metallographic analyses of unirradiated and irradiated (Zry-2) samples tested at ≈1200˚C give oxide layer thicknesses (Zry-2 and Zry-4) and weight gains (Zry-2) determined from the metallography that are in excellent agreement with the Cathcart-Pawel model predictions. Determination of weight gain from metallographic analysis of the irradiated samples tested at ≈1000˚C and ≈1100˚C is in progress. Based on preliminary analyses, the weight gain determined from metallography of the high burnup Zry-2 tested at ≈1200˚C is within 10% of the Cathcart-Pawel model predictions. The main difference observed between the characteristics of unirradiated and irradiated samples oxidized at ≈1200˚C is the presence of non-uniform alpha/beta interfaces in irradiated cladding leading to larger (≈45%) oxygen-stabilized alpha regions formed at high temperature and the presence of alpha-prime islands formed within the beta layer during cooling. Although the increased thickness of the brittle oxygen-stabilized alpha and alpha-prime regions has little impact on weight gain, it may have a detrimental effect on ECCS quench and post-quench performance by reducing the thickness of the ductile beta layer.

The oxidation tests completed thus far with irradiated cladding are with samples having pre-test outer-surface oxide layers of ≈10 μm (Limerick) and ≈30 μm (TMI-1) and corresponding hydrogen levels of ≈70 wppm and ≈150 wppm. Completion of the high burnup PWR cladding tests will broaden this range to in-reactor-formed oxide layers of ≤100 μm and hydrogen contents of ≤500 wppm. This range is more than adequate to characterize the oxidation kinetics of high burnup BWR and PWR Zircaloy cladding.

References

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